(12) EUROPEAN PATENT APPLICATION

(71) Applicant: CELANESE CORPORATION
1211 Avenue of the Americas
New York New York 10036(US)

(72) Inventor: Gerberich, Harold R.
4814 Augusta Drive
Corpus Christi Texas(US)

(74) Representative: De Minvielle-Devaux, Ian Benedict
Peter et al,
CARPMAELS & RANSFORD 43, Bloomsbury Square
London WC1A 2RA(GB)

(54) Process for producing aromatic diols and their ester and ether derivatives.

(57) Carboxylate esters of aromatic diols, e.g., the monoacetate ester of hydroquinone, and carboxylate esters of monoalkyl ethers of aromatic diols, e.g, p-methoxyphenyl acetate, are produced by subjecting an aromatic ketone containing a hydroxy, alkoxy or acyloxy radical on the aromatic ring, e.g.4-hydroxyacetophenone, to a Baeyer-Villiger oxidation using peracetic acid as oxidant under conditions such that the reaction mass contains no more than about 0.1 wt.% of sulfuric acid based on the weight of the initially added pure peracetic acid. The carboxylic esters may be hydrolyzed to the aromatic diols, e.g., hydroquinone, or to the monoalkyl ethers of the aromatic diols, e.g. the monomethyl ether of hydroquinone.

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PROCESS FOR PRODUCING AROMATIC DIOLS
AND THEIR ESTER AND ETHER DERIVATIVES

This invention relates to a process for the production of certain aromatic diol derivatives (of the class of carboxylate ester and monoalkyl ether derivatives) and aromatic diols themselves.

Aromatic diols such as hydroquinone are known commodities of commerce having use, for example, as photographic developers, polymerization inhibitors, dye intermediates and anti-oxidants.

Hydroquinone (HQ) has been commercially produced by the manganese oxide-catalyzed oxidation of aniline to quinone followed by the iron-catalyzed reduction of the quinone to hydroquinone. A more recently developed method of producing hydroquinone comprises the diisopropylation of benzene to form para-diisopropylbenzene followed by peroxidation of the latter compound and acid-catalyzed decomposition of the diperoxide to produce hydroquinone and acetone. While there are advantages in each of these processess, a process of making aromatic diols such as hydroquinone which involved a lower cost of construction of a commercial unit and/or a lower operating cost of production would be highly desirable.

The carboxylate esters and monoalkyl ethers of aromatic diols are also known. In addition to some of the same uses mentioned for aromatic diols, these compounds have use as bactericides and antiseptics, pharmaceuticals e.g. as expectorants and depigmentors, and fragrances.

Aromatic diols and their dicarboxylate esters, e.g. the diacetate ester of hydroquinone (DAHQ), have also found application as monomers in the preparation of certain polymers, e.g. those capable of forming an anisotropic melt phase and suitable for being formed into shaped articles such as molded articles, fibers and films as described, for example, in U.S. Patents Nos. 4,330,457; 4,351,918; and 4,355,132.

With regard to the process disclosed and claimed
herein, the oxidation of ketones with peroxy compounds to
form esters, i.e. the "Baeyer-Villiger" reaction, is known.
Some references with disclosures of examples of this type
5   of reaction and descriptions of their teachings are as
follows:

Hirao et al, Koen Yoshishu- Koryo, Terupen oyobi
Seiyu Kagaku ni kansuru Toronkai, 23rd 1979, 131-3 (Japan).
Chem.Soc. Japan : Tokyo,Japan, as abstracted in C.A. 93,
10   7777n, (1980) show the Fries rearrangement of phenyl acetate
and Friedel-Crafts acetylation of phenol to form para-hydroxy
-acetophenone which is then oxidized with hydrogen peroxide
using sulfuric acid as catalyst to para-hydroxyphenyl acetate;
the latter is then hydrolyzed with sulfuric acid in acetic
15   acid to yield hydroquinone.

Von E. Doering et al, Journal of the American
Chemical Society 72, 5515-5518 (1950) teach the Baeyer-
Villiger oxidation of various aromatic ketones, including
acetophenone and para-substituted benzophenones, to esters
20   using peracetic acid as the oxidant and show that sulfuric
acid has a "marked catalytic action" with regard to the
yield and reaction time (page 5517,col.1).

Ogata et al, Journal of Organic Chemistry 43,
No. 12, 2417-2419 teach the Baeyer-Villiger oxidation of
25   acetophenone and substituted acetophenones to the corres-
ponding aryl acetates using permonophosphoric acid as
oxidant and sulfuric acid as catalyst and show that the
reaction rate is highly dependent on the acidity of the
solution.
30
Starcher et al, Journal of the American Chemical
Society, 80, 4079-4082 (1958) teach the synthesis of lactones
by means of the Baeyer-Villiger oxidation of cyclic ketones
using peracetic acid as oxidant. In the paragraph bridging
35   pages 4079 and 4080, the authors state: " The absence of
inorganic impurities, notably water, hydrogen peroxide,
mineral acids and salts, reduced polymerization to a minimum
during the reaction step and avoided.many of the by-products
which plagued previous investigators."

Adam et al, Journal of Organic Chemistry, 44, No. 26, 4969 (1979) describe the use of bis(trimethylsilyl) monoperoxysulfate as a Baeyer-Villiger oxidant in the oxidation of ketones to their corresponding esters. The authors state that the shortcomings of a previously-used oxidant for this purpose, Caro's or monoperoxysulfuric acid, are "(i) the use of aqueous conditions, (ii) the presence of strong acid and (iii) undesirable side reactions."

In addition to Hirao et al discussed previously, other references showing the formation of hydroxyaromatic ketones by the Fries rearrangement of aromatic esters or the Friedel-Crafts acylation of phenols are also in the literature. The following are some of these references with summaries of their teachings:

Lewis, U.S. Patent No. 2,833,825 shows the rearrangement of phenyl or other aromatic esters to acyl-phenols or other hydroxy aromatic ketones using anhydrous hydrogen fluoride as catalyst. The examples of this patent are limited to the rearrangement of esters of higher fatty acids with the yields ranging from 55 to 95%.

Simons et al, Journal of the American Chemical Society, 62, 485 and 486 (1940) show the use of hydrogen fluoride as a condensing agent for various rearrangements and at page 486 show the Fries rearrangement of phenyl acetate to obtain p-hydroxyacetophenone.

Dann and Mylius in a dissertation included as part of a series of Reports from the Institute for Applied Chemistry of the University of Erlangen, received for publication on January 7, 1954 and published in Annalen der Chemie 587 Bank, pages 1 to 15, show the rearrangement of phenyl acetate in hydrogen fluoride to 4-hydroxyacetophenone, with a maximum yield of 81% after 24 hours of reaction time, and report a yield of 92% stated to be obtained by K. Weichert as reported in Angewandte Chemie 56, 338 (1943), However, Dann and Mylius suggest that the difference in yields may

be at least partly due to the previous ignoring by Weichert
of the accompanying 2-hydroxyacetophenone. Dann and Mylius
also report somewhat lower yields of hydroxy aromatic ketones
from rearrangements in hydrogen fluoride of m-cresyl acetate,
p-cresyl acetate, and guaiacol acetate.

Dann and Mylius also disclose the reaction of
phenol and glacial acetic acid in the presence of hydrogen
fluoride to produce 4-hydroxyacetophenone in a yield of
61.6%. This reaction may be conventionally characterized
as a Friedel-Crafts actylation of phenol with acetic acid
as the acetylating agent.

Simons et al, Journal of the American Chemical
Society, 61, 1795 and 1796 (1939) teach the acylation of
aromatic compounds using hydrogen fluoride as a condensing
agent and in Table 1 on page 1796 show the acetylation of
phenol with acetic acid to produce p-hydroxyacetophenone
in 40% yield.

Meussdoerffer et al, German Offenlegungsschrift
26 16 986 published October 27, 1977 and assigned to Bayer
AG, disclose the acylation of phenolic compounds such as
phenol itself with an acyl halide such as acetyl chloride
to form hydroxy aromatic ketones.

In accordance with this invention, a product
comprising a major proportion of a carboxylate ester of
an aromatic diol, e.g. the monoacetate of hydroquinone
(MAHQ), or a carboxylate ester of a monoalkyl ether of an
aromatic diol, e.g. 4-acetoxyanisole, is produced by
subjecting an aromatic ketone, containing a hydroxy, alkoxy
or acyloxy radical on the aromatic ring, e.g.4-hydroxy-
acetophenone (4-HAP), to a "Baeyer-Villiger" oxidation
using as oxidant peracetic acid under conditions such that
the reaction mass contains no more than 0.1 weight percent
of sulfuric acid based on the weight of the initially added
pure peracetic acid.

Preferably, the reaction mass also contains no
more than 5 weight percent of water based on the weight of
pure peracetic acid initially added.

It is essential to this invention that there be
<u>not</u> used the commercial peracetic acid solutions which
contain sulfuric acid in an amount greater than the
maximum amount defined herein and which also contain more
than the preferred maximum amount of water defined herein,
unless these commercially available solutions are subjected
to treatment so that their contents of sulfuric acid and
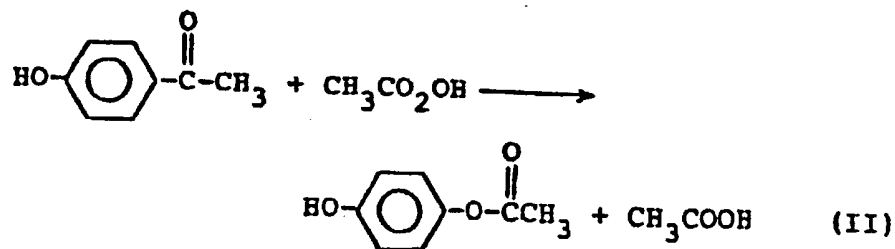water are appropriately reduced.

This invention also contemplates the hydrolysis
of carboxylate esters of the aromatic diols, e.g, MAHQ, to
obtain unmodified aromatic diols, e.g. hydroquinone (HQ),
or monoalkyl ethers of aromatic diols.

The Baeyer-Villiger oxidation contemplated by
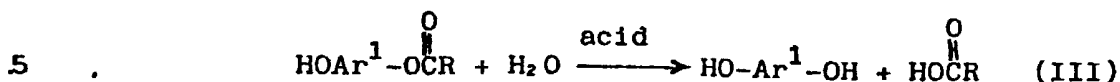this invention proceeds as in equation (I):

$$YO-Ar^1-\overset{\overset{O}{\|}}{C}R + CH_3CO_2OH \longrightarrow YO-Ar^1-O\overset{\overset{O}{\|}}{C}R$$
$$+CH_3COOH \quad (I)$$
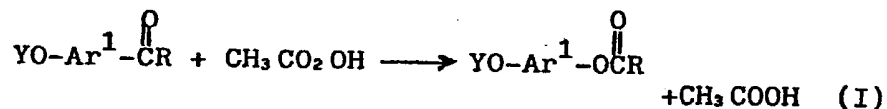
where R is an alkyl radical, Ar^1 is a divalent aromatic
radical,(both more specifically defined below), and Y is
hydrogen ,R, or $R\overset{\overset{O}{\|}}{C}-$.

If the <u>monoacetate ester of hydroquinone</u> (MAHQ)
is the desired product, the reaction proceeds as in equation
II:

$$HO-\underset{}{\bigcirc}-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3CO_2OH \longrightarrow$$
$$HO-\underset{}{\bigcirc}-O-\overset{\overset{O}{\|}}{C}CH_3 + CH_3COOH \quad (II)$$

If a monocarboxylate ester of an aromatic diol,
is the product of the Baeyer-Villiger oxidation, it may be
hydrolyzed to the aromatic diol as shown in equation (III):

$$HOAr^1\text{-}OCR + H_2O \xrightarrow{acid} HO\text{-}Ar^1\text{-}OH + HOCR \quad (III)$$

When it is desired to produce HQ from MAHQ, the
hydrolysis reaction proceeds as in equation (IV):

$$HO\text{-}\bigcirc\text{-}O\text{-}CCH_3 + H_2O \longrightarrow$$
$$HO\text{-}\bigcirc\text{-}OH + HOOCCH_3 \quad (IV)$$
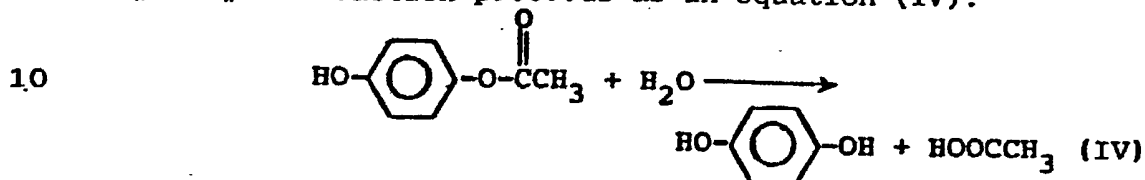
In equations I and III, Ar^1 is a divalent aromatic
radical. The specific nature of the radical is not critical
but it is preferably a radical resulting from the removal of
two ring hydrogen atoms from benzene, naphthalene, or biphenyl,
either unsubstituted or with ring hydrogens substituted with
radicals such a methyl, tolyl; and appropriately masked amino,
or sulfhydryl substituents. Ar^1 is preferably 1,4-phenylene,
2,1-naphthylene, 2,6-naphthylene, 5-phenyl-1,2-phenylene,
3-phenyl-1,4-phenylene or 3-methyl-1, 4-phenylene with the
ketocarbon and corresponding groups occupying the first
stated numbered position of Ar^1 when the positions are not
equivalent. Most preferably Ar^1 is 1,4-phenylene.

The R groups in equations (I) and (III) are alkyl
groups containing, for example, 1 to 18 carbon atoms, pre-
ferably 1 to 4 carbon atoms, and may be the same or different.
More preferably, R is methyl, ethyl or propyl and most pre-
ferably methyl corresponding to the use of methyl ketones and
others and acetate esters in the latter equations. The pre-
ferred products are the monoacetate ester of hydroquinone
(MAHQ) formed by the Baeyer-Villiger oxidation of 4-hydroxy-
acetophenone (4-HAP) and hydroquinone (HQ) formed by the
hydrolysis of the MAHQ.

The aromatic ketone used to form the carboxylate ester of an aromatic diol or the carboxylate ester of a monoalkyl ether of an aromatic diol may be prepared by any method known in the art. For example, a hydroxy aromatic ketone may be prepared by the Fries rearrangement of the corresponding aromatic ester as indicated by equation (V) where Ar^1 and R have the definitions given above and Ar is an aryl radical corresponding to the definition of Ar^1 given above except that the carbon bonded to hydroxy,alkoxy or acyloxy group as shown in equation (I) is bonded to a hydrogen instead.

$$\text{ArOCR} \xrightarrow{\text{catalyst}} \text{HO-Ar}^1\text{CR}, \qquad (V)$$
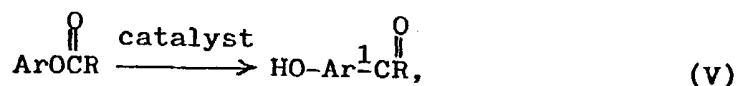
Alternatively, a phenolic compound and an acylating agent may be reacted in a Friedel-Crafts acylation to form the hydroxy aromatic ketone, in accordance with the following equation :

$$\text{ArOH} + \text{R-C-X} \xrightarrow{\text{catalyst}} \text{HO-Ar}^1\text{-C-R} + \text{HX} \qquad (VI)$$
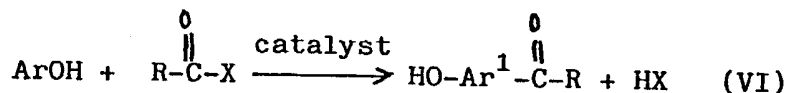
where Ar, Ar^1 and R have the meanings given previously and X in equation (VI) is the residue minus the aryl group, R-C-,of compounds which are known acylating agents. X may be, for example, hydroxy, acyloxy, e.g., acetoxy; and halide, e.g., fluoride,chloride, and bromide. Examples of phenolic compounds which may be employed are phenol, 1-naphthol, 2-naphthol, 2-phenylphenol, 4-phenyl-phenol and o-cresol. Acylating agents which may be used are for example alkanoic acids, e.g., acetic and propionic acids, alkanoic acid anhydrides, e.g., acetic and propionic anhydrides, and acyl halides, e.g. acetyl and propionyl fluorides,chlorides, and bromides. It is to be noted that, although the reaction of a phenolic compound and an acylating agent is characterized herein as a "Friedel-Crafts acylation", no opinion as to the mechanism of reaction is implied by this characterization.

Th.e catalyst for both of the foregoing reactions is prefer-
ably hydrogen fluoride but any other catalyst known in the
art to be effective for the Fries and Friedel-Crafts
reactions may be used,e.g. aluminum chloride, zinc chloride,
5   or boron trifluoride.

        In carrying out the reaction, the aromatic ester
or phenolic compound and acylating agent, catalyst, and if
desired (when an aromatic ester is the starting material)
an additive for the reaction (such as acetic anhydride or
10   acetic acid) may be charged into a corrosion-resistant
reactor and the mixture maintained at a temperature, for
example, of 20 to 150° C for a period, for example, of ½ to
4 hours ,at a pressure, for example, of 25 to 500 psig (273.7
to 3548.8 kPa). If HF is used as the catalyst it may be
15   charged as a liquid or a gas using well known handling methods.

        In carrying out the reaction,an inert gas such as
nitrogen may be used to keep the reaction space under the
desired pressure and sufficient HF in contact with the react-
ing liquid. An excess of HF is generally used, for example,
20   7 to 75 moles per mole of aromatic ester of phenolic compound
initially present in the reaction zone. If MAHQ is the
desired product of the reaction, the starting material if a
Fries rearrangement is employed will be phenyl acetate, while
phenol and an acetylating agent such as acetic acid or acetic
25   anhydride are the starting material if a Friedel-Crafts
acylation is utilized. In both cases, the starting material
is converted to 4-HAP which is in turn converted by the process
of this invention to MAHQ.

30   If a monoalkyl ether of an aromatic diol or the
carboxylate ester of such ether is the desired product, the
monoalkyl ether of the hydroxy aromatic ketone is first
prepared using any of the techniques known in the art, e.g.,
reaction of the hydroxy aromatic ketone,e.g. 4-HAP, with an
35   alkyl iodide such as methyl iodide under basic conditions.

If a diester of an aromatic diol, e.g. the
diacetate ester of hydroquinone (DAHQ), is desired as the
end product, a hydroxy aromatic ketone such as 4-HAP may
first be acylated, e.g. with acetic anhydride. (Such a
method is described in our European Patent Application
85305222.3). The resulting acyloxy aromatic ketone, e.g.,
4-acetoxyacetophenone (4-AAP), may then be subjected to a
Baeyer-Villiger oxidation in accordance with this invention
to produce a diester of an aromatic diol, e.g. DAHQ.

In producing esters of aromatic diols and esters
of monoalkyl ethers of aromatic diols in accordance with
equation (I), the aromatic ketone (e.g. the hydroxy aromatic
ketone resulting from the previously described Fries re-
arrangement or Friedel-Craft acylation) or a monoalkyl ether
or monoester of such hydroxy aromatic ketone, is subjected
to a Baeyer-Villiger oxidation by reacting the ketone with
peracetic acid under such conditions that the reaction
solution contains no more than 0.1 wt.%, preferably no more
than 0.05 wt.% of sulfuric acid based on the weight of pure
peracetic acid initially added. Advantageously the reaction
solution does not contain more than 5 wt % (preferably not
more than 2 wt.%) of water, based on the weight of pure
peracetic acid. In general, the less the sulfuric acid and
water present the better. The reaction solution may there-
fore be substantially free of sulfuric acid and/or water.
A solvent for the hydroxy aromatic ketone may also be used
in the initial reaction solution, e.g., an alkanoic acid
such as glacial acetic acid or formic acid. Preferably,
the peracetic acid is added in the form of a solution con-
sisting essentially of 5 to 45 wt.% peracetic acid and
the remainder a solvent such as acetic acid, methyl acetate,
ethyl acetate, acetone or a mixture of any thereof.

The amount of peracetic acid supplied to the
reaction is generally in the range for example of 0.5 to
2 moles per mole of aromatic ketone. The reaction may
be carried out at a temperature, for example, of 20 to
140° C and a pressure, for example, of 25 mm of mercury
to 2 atmospheres for a period, for example, of 0.5 to
3 hours.

An alternative method of producing diesters such as DAHQ is simply to subject the monoester, e.g., MAHQ, resulting from the Baeyer-Villiger oxidation of hydroxy aromatic ketones e.g. 4-HAP, in accordance with this invention, to an acylation or esterification for example using techniques well-known in the art.

The following Examples further illustrate the invention.

Examples 1 to 5 illustrate the preparation of intermediates.

Example 1

This Example illustrates the preparation of 4-hydroxyacetophenone by the Fries rearrangement of phenyl acetate using hydrogen fluorides as catalyst.

Into a 300 cc Hastelloy C autoclave was charged 40.8 g (0.3 mol) of phenyl acetate. The autoclave was sealed, immersed in a dry-ice/isopropanol bath and cooled internally to -45°C, and evacuated to ca. 100 Torr. 120 g (6.0 mol) of anhydrous hydrogen fluoride was added in a manner such that the internal temperature of the autoclave did not exceed 0° C. The internal pressure of the reactor was then adjusted to 0 psig (101.325 kPa) with nitrogen. The contents of the autoclave were stirred and heated to 75°C for 1 hour. The hydrogen fluoride was vented over a 45 minute period at ca. 45° C. The mixture was poured onto 25 g of ice and neutralized with 45% potassium hydroxide solution. The aqueous mixture was extracted with ethyl acetate. The organic fraction was then dried over anhydrous magnesium sulfate and filtered, and the solvent was removed on a rotary evaporator to yield 44.0 g of a dark green solid corresponding to 99.9% conversion of phenyl acetate and 94.3% selectivity to 4-hydroxyacetophenone.

Example 2

This Example illustrates the preparation of 4-hydroxyacetophenone by the Fries rearrangement of phenyl acetate using hydrogen fluoride as catalyst with acetic anhydride as additive.

Into a 300 cc Hastelloy C autoclave were charged 50.6 grams (0.5 mole) of acetic anhydride. The autoclave was cooled to -50°C and evacuated to 5 Torr whereupon 120 g (6.0 mole) of anhydrous hydrogen fluoride were transferred from a cylinder to the autoclave. After the transfer of hydrogen fluoride had been completed, the internal temperature and the internal pressure of the autoclave were adjusted to -50°C and 0 psig (101.325 kPa) using nitrogen, respectively. Into the stirred autoclave were added 81.6 g (0.6 mol) of phenyl acetate at such a rate that the temperature of the mixture did not exceed -23°C. Upon completion of phenyl acetate addition, the contents were warmed to 50°C and stirred for 3 hours during which time a pressure of ca. 40 psig (377.125 kPa) was generated. At the end of the run, the hydrogen fluoride was vented through a caustic scrubber and the contents of the autoclave were poured onto ca. 30 g of ice. The pH of the mixture was adjusted to 6.5 using 45% potassium hydroxide and the mixture was then extracted with 75 ml of ethyl acetate (3x). The organic solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed using a rotary evaporator.

The reaction proceeded with 98.1% conversion of phenyl acetate and with the following selectivities: phenol, 1%; 4-hydroxyacetophenone (4-HAP), 82.3%; 2-hydroxyacetophenone (2-HAP), 4.3%; 3-hydroxyacetophenone (3-HAP), 0.1%; 4-acetoxy-acetophenone (4-AAP), 3.8%; and 4-(4'-hydroxyphenyl)-acetophenone (HPAP), 0.4%.

Example 3

This Example illustrates the formation of 4-hydroxyacetophenone by the Fries rearrangement of phenyl acetate using hydrogen fluoride as catalyst and acetic acid as additive.

The procedure for Example 2 was repeated except that 18 grams (0.3 mole) of acetic acid rather than acetic anhydride were charged into the reactor before it was cooled and charged with the hydrogen fluoride. A conversion of 99.0% of phenyl acetate was obtained with the following selectivities:
phenol, 3.3%; 4-HAP, 80.8%; 3-HAP, 0; 2-HAP, 5.8%; 4-AAP, 0.3%; and HPAP, 0.3%.

Example 4

This Example illustrates the preparation of 4-hydroxyacetophenone (4-HAP) by the Friedel-Crafts acetylation of phenol with acetic acid as the acetylating agent.

Phenol (9.4 g, 0.1 moles) and acetic acid (12.0 g, 0.2 moles) were charged into a 300 ml Hastelloy C autoclave at room temperature. The reactor was evacuated and cooled to -20°C. HF (100 g, 5 moles) was then transferred into the reactor. The reactor was heated to 80°C and maintained for 1 hour at reaction temperature. At the end of the reaction the reactor was cooled to 20°C and the excess HF was vented to a KOH scrubber. Ethyl acetate was added to the contents of the reactor. The mixture was then neutralized with 45% aqueous KOH. The resulting organic phase was separated, dried over MgSO$_4$ and evaporated to afford a yellow solid which contained 13.1 g (0.096 moles) of 4-HAP.

Example 5

This Example illustrates the preparation of 4-hydroxyacetophenone by the Friedel-Crafts acetylation of phenol with acetic anhydride as the acetylating agent.

Into a 300 cc Hastelloy C autoclave cooled to -20 to   °C and evacuated to 50 Torr were charged 150 g (7.5 mole) of anhydrous hydrogen fluoride. The content of the autoclave was warmed to 50°C resulting in an internal pressure of 25 psig (273.7 kPa). A solution of 23.5 g (0.25 mole) of phenol and 25.5 g of acetic anhydride was added to the autoclave over a 3 minute period causing the pressure to drop to 14 psig (197.855). The solution was stirred for 1 hour at 50°C whereupon the hydrogen fluoride was vented at the reaction temperature. The contents of the autoclave were poured onto ice and the aqueous phase was adjusted to pH 6.0 with a 45% solution of potassium hydroxide. The aqueous phase was extracted with 75 ml of ethyl acetate (3x); the organic fractions were combined, dried over anhydrous magnesium sulfate, and filtered. The reaction proceeded with 99% conversion based on phenol and 95% selectivity to 4-hydroxyacetophenone.

The procedure of Examples 1 to 5 can also be used to produce, with high conversions and selectivities, 1-hydroxy-2-acetonaphthone from 1-naphthyl acetate; 6-hydroxy-2-acetonaphthone from 2-naphthyl acetate; 2-hydroxy-5-phenylacetophenone from 4-phenylphenyl acetate; 4-hydroxy-3 - phenylacetophenone from 2-phenylphenyl acetate; and 4-hydroxy-3-methylacetophenone from 0-cresyl acetate.

Examples 6 to 12 illustrate the conversion of 4-hydroxy-acetophenone (4-HAP) to the monoacetate ester of hydroquinone by the Baeyer-Villiger oxidation, using peracetic acid as the oxidizing agent under conditions defined by this invention.

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Example 6

To 650 grams of commercially available peracetic
acid were slowly added 650 grams of acetic anhydride. This
commercial acid contained ca. 40 wt.% peracetic acid, ca. 13
.5   wt.% water, ca.5 wt.% hydrogen peroxide and ca. 1 wt.% sul-
furic acid, and the purpose of the acetic anhydride treat-
ment was to convert the water and hydrogen peroxide present
to acetic acid and peracetic acid, respectively. The solu-
tion was cooled and stirred during the addition to maintain
10   the temperature at below 30°C. This solution was then
distilled under vacuum(20-30 mmHgA, ca.40°C) through a one-
inch Vigreux column. The initial 20cc. of distillate were
discarded. Then, ca 1000 cc. of material was distilled with-
out reflux. This material referred to below as "purified
15   peracetic acid solution" contained ca.27 wt.% peracetic acid
and ca. 73 wt.% acetic acid and was used for the oxidations
in this and the following Examples.

In a solution of 60 grams of glacial acetic acid
and 10 grams of acetic anhydride were dissolved 30 grams of
20   4-HAP. This solution was placed into a 250 cc. three-neck
flask. While heating the solution ot 60°C, the flask was
partially evacuated to a pressure of 60 mmHgA. This pressure
was maintained throughout the experiment. To the solution
were added 77.5 grams of the purified peracetic acid solution
25   containing 20.46 g of pure peracetic acid, fed dropwise over
a period of 40 minutes, and the solution was heated for an
additional 80 minutes. The initial mole ratio of peracetic
acid to 4-HAP was 1.22. The solution was then cooled and
analyzed by gas chromatography and other well-established
30   procedures.

The product solution weighed 171.3 grams and
contained 18.0 wt % monoacetate ester of hydroquinone (MAHQ),
0.47 wt% diacetate ester of hydroquinone (DAHQ), 0.03 wt %
hydroquinone (HQ), 0.05 wt% benzoquinone (BQ), 0.17 wt%
35   4-acetoxyacetophenone (4-AAP), and 0.41 wt% of 4-hydroxy-
acetophenone (4-HAP). Peracetic acid was not detected.
This corresponds to 97% conversion of 4-HAP and 97% efficiency
to hydroquinone and its esters.

Example 7

The procedure of Example 6 was followed except that the temperature employed was 80°C, the solvent consisted of 70 g acetic acid (and no acetic anhydride) to which 4.4 mg of ethylene diamine tetraacetic acid (EDTA) were added and 51.7 grams of purified peracetic acid solution containing 13.65 of pure peracetic acid were fed over the 40 min. period. The initial mole ratio of peracetic acid to 4-HAP was 0.81.

The product solution weighed 154.0 grams and contained 13.7 wt.% MAHQ, 0.33 wt.% DAHQ, 0.78 wt.% HQ, 0.03 wt% BQ, and 4.8 wt% of 4-HAP, corresponding to 74.93% conversion of 4-HAP and 92.17% efficiency to HQ and its esters.

Example 8

The procedure of Example 6 was followed except that the solvent consisted of 70 grams of acetic acid and no acetic anhydride, to which 4.4 mg of EDTA were added, and the purified peracetic acid solution was added over a 10 minute period and the reaction solution was heated for an additional 40 minute period. The initial mole ratio of peracetic acid to 4-HAP was 1.22.

The product solution weighed 177.3 grams and contained 16.8 wt% MAHQ, 0.26 wt% of DAHQ, and 0.13 wt.% HQ, 0.13 wt.% BQ and 0.02 wt.% 4-HAP, corresponding to 99.88% conversion of 4-HAP and 90.97% efficiency to HQ and its esters.

Example 9

The procedure of Example 7 was followed except that 51.7 grams of purified peracetic acid solution containing 14.37 grams of peracetic acid were fed over a 20 minute period, the solution was heated for an additional 40 minutes and the solvent consisted of 60 grams of acetic acid and 10 grams of acetic anhydride. The initial mole ratio of peracetic acid to 4-HAP was 0.86.

The product solution weighed 153.0 grams and contained 14.10 wt% MAHQ, 1.10 wt.% DAHQ, 0.77 wt.% HQ, 0.08 wt.% BQ and 4.60 wt.% 4-HAP corresponding to 75.41% conversion of 4-HAP and 97.97% efficiency to HQ and its esters.

Example 10

The procedure of Example 6 was followed except that 62.1 grams of purified peracetic acid solution containing 17.26 grams of peracetic acid were fed over a 30 minute period, the solution was heated for an additional 30 minutes, and the solvent consisted of 70 grams of acetic acid to which was added 0.1 gram of sodium acetate. The initial mole ratio of peracetic acid to 4-HAP was 1.03.

The product solution weighed 161.7 grams and contained 21.40 wt.% MAHQ, 0.00 wt.% DAHQ, 0.02 wt.% HQ, 0.00 wt.% BQ and 0.55 wt.% 4-HAP corresponding to a conversion of 4-HAP of 97.04% and an efficiency to HQ and its esters of 100%.

Example 11

The procedure of Example 6 was followed except that 107.4 grams of purified peracetic acid solution containing 29.11 grams of peracetic acid were fed over a 30 minute period, the solution was heated for an additional 30 minutes and the 4-HAP solution consisted of 50.8 grams of acetic acid and 50.8 grams of 4-HAP. The initial mole ratio of peracetic acid to 4-HAP was 1.04.

The product solution weighed 206.9 grams and contained 21.9 wt.% MAHQ, 0.09 wt.% DAHQ, 0.01 wt.% BQ, 0.01 wt.% HQ and 1.70 wt.% 4-HAP corresponding to a normalized conversion of 4-HAP based on 88.85% accountability of products of 91.69% and a normalized efficiency to HQ and its esters of 99.9%.

Example 12

The procedure of Example 6 was followed except that 90.8 grams of purified peracetic acid solution containing 24.61 grams of peracetic acid were fed over a 30 minute period, the solution was heated for an additional 30 minutes and the 4-HAP solution consisted of 69.1 grams of 90% formic acid and 40.3 grams of 4-HAP. The initial mole ratio of peracetic acid to 4-HAP was 1.09.

The product solution weighed 198.5 grams and contained 17.6 wt.% MAHQ, 0.17 wt.% DAHQ, 0.85 wt.% HQ, 0.04 wt.% BQ and 1.10 wt % 4-HAP corresponding to a normalized conversion of 4-HAP based on 88.99% accountability of products of 93.91% and a normalized efficiency to HQ and its esters of 99.70%.

In comparative Examples A, B and C, 0.5 ml of concentrated sulfuric acid was added to the 4-HAP solution to determine the effect of the presence of a small amount of sulfuric acid such as that present in commercial peracetic acid solutions or used to catalyze Baeyer-Villiger oxidations.

Comparative Example A

The procedure of Example 6 was followed except that the reaction temperature was 80°C, the 4-HAP solution contained 0.5 ml. of concentrated sulfuric acid and 4,40 mg. of EDTA, 77.5 grams of purified peracetic acid solution containing 21.54 grams of peracetic acid were fed over a 20 minute period and the solution was heated for an additional 100 minutes. The initial mole ratio of peracetic acid to 4-HAP was 1.28.

The product solution weighed 178.40 grams and contained 1.70 wt.% MAHQ, 0.21 wt.% DAHQ, 3.30 wt.% HQ, 0.01 wt.% BQ and 4.10 wt.% 4-HAP, corresponding to a coversion of 4-HAP of 71.67% and an efficiency to HQ and its esters of 47.70%.

Comparative Example B

The procedure of Example 7 was followed except that the temperature of reaction was 60°C, the 4-HAP solution contained 0.5 ml. of concentrated sulfuric acid, the purified peracetic acid solution was fed over a 20 minute period and no EDTA was employed.

The product solution weighed 148.60 grams and contained 2.00 wt.% MAHQ, 2.30 wt.% DAHQ, 7.00 wt.% HQ, 0.00 wt.% BQ and 6.80 wt.% 4-HAP, corresponding to a conversion of 4-HAP of 64.27% and an efficiency to HQ and its esters of 92.91%.

Comparative Example C

The procedure of Example 9 was followed except that the reaction temperature was 60° C, then 4-HAP solution contained 0.5 ml. of concentrated sulfuric acid and 4.4 mg. EDTA, the paracetic acid was fed over a 40 minute period, and the solution was heated for an additional 20 minute period.

The product solution weighed 153.20 grams and contained 3.10 wt.% MAHQ, 0.31 wt.% DAHQ, 0.03 wt.%BQ and 5.00 wt.% 4-HAP corresponding to a conversion of 4-HAP of 64.32% and an efficiency to HQ and its esters of 67.92%.

A comparison of the results obtained in Examples 6,7 and 9, wherein no sulfuric acid was present in the reaction, with those obtained in comparative examples A,B and C wherein a small amount of sulfuric acid was present comparable to that present in commercial peracetic acid solutions or added as a catalyst in Baeyer-Villiger oxidations, indicates that the absence of any appreciable amount of sulfuric acid has an unexpectedly positive effect on the oxidation of hydroxy aromatic ketones such as 4-HAP, to aromatic diols and their esters, such as MAHQ, DAHQ and HQ, both with regard to the conversion of the ketone and efficiency to the diols and their esters.

The following comparative Example D illustrates the effect of an appreciable amount of water in the oxidation reaction solutions.

Comparative Example D

The procedure of Example 10 was followed except that 10 grams of water were added to the 4-HAR solution and no sodium acetate was added.

The product solution weighed 167.00 grams and contained 21.10 wt.% MAHQ, 0.00 wt.% DAHQ, 0.13 wt.% HQ, 0.00 wt.% BQ and 1.30 wt.% HAP corresponding to a conversion of 4-HAP of 92.76% and an efficiency to HQ and its esters of 100%.

Comparison of the results of comparative Example D with those of Example 10 shows that the presence of an appreciable amount of water in the reaction has the effect of reducing somewhat the conversion of the hydroxy aromatic ketone to the diol ester.

Comparative Examples E and F illustrate the effect of using hydrogen peroxide rather than peracetic acid as the oxidant.

Comparative Example E

The procedure of Example 11 was followed except that 26.6 grams of a hydrogen peroxide solution described in comparative Example E were used as the oxidant in place of the peracetic acid solution and the 4-HAP solution consisted of 53.2 grams of 90% formic acid and 30.0 grams of 4-HAP. The initial mole ratio of hydrogen peroxide to 4-HAP was 1.09.

The product solution weighed 105.2 grams and contained 6.00 wt.% MAHQ, 0.0 wt.% DAHQ, 8.10 wt.% HQ, 0.0 wt. % BQ, and 5.00 wt.% 4-HAP corresponding to a normalized conversion of 4-HAP of 75.47% and a normalized efficiency to HQ and its esters of 100.00% based on 71.48% accountability of products.

Comparison of the results of Comparative Examples E and F with thos of Examples 11 and 12 indicates that the use of peracetic acid in the absence of sulfuric acid as oxidant yields higher conversions of 4-HAP than hydrogen peroxide with equivalent efficiencies to HQ and its esters.

Example 13

This Example illustrates the hydrolysis of MAHQ and DAHQ to HQ.

Product from several experiments as described in Example 6 were combined and most of the acetic acid removed by evaporation under vacuum at 100°C. Analysis of the non-volatile portion showed that it contained 81.5 wt.% MAHQ,2.0 wt.%HQ, 2.2 wt.% DAHQ, 1.5 wt.% 4-HAP, 0.01 wt.% BQ, and 1.2 wt.% acetic acid. 40.0 grams of this non-volatile material were added to a solution of 0.4 gram of 37 wt.% hydrochloric acid in 40.0 grams of water and heated for two hours at 85°C. Upon cooling in ice-water a crystalline solid precipitated. The solid was filtered, washed with water, and dried in a vacuum desiccator. The dried solid weighed 14.02 grams and contained 97.7 wt.% HQ.0.05 wt.% MAHQ, 0.0 wt.% DAHQ, 0.58 wt. % BQ, 2.4 wt.% acetic acid, 0.55 wt.% water, and 0.0 wt.% 4-HAP. The filtrate plus wash weighed 99.42 grams and contained 11.3 wt.% HQ, 0.10 wt.% MAHQ, 0.02 wt.% DAHQ, 17.0 wt.% acetic acid, 70.6 wt.% water, 0.01 wt.% BQ, and 0.23 wt.% 4-HAP. These results show that of the total MAHQ, DAHQ , and HQ fed (0.2263 mole) 99.4% (0.2249 mole) was recovered as HQ in the solid and filtrate.

Example 14

This Example illustrates the Baeyer-Villiger oxidation of 4-acetoxyacetophenone (4-AAP) to primarily DAHQ.

The procedure of Example 6 was followed except that 15.0 grams of 4-AAP were dissolved in 50 grams of acetic acid (no acetic anhydride), the temperature employed was 80° C,26.1 grams of purified peracetic acid solution were added over a 30 minute period, and the reaction solution was heated for an additional 30 minute period. The initial mole ratio of peracetic acid to 4-AAP was 1.10.

The product solution weighed 91.0 grams and contained 2.84 wt.% DAHQ, 0.01 wt.% MAHQ, 0.03 wt.% HQ, 0.01 wt.% BQ, 14.31 wt.% 4-AAP, and 5.42 wt.% peracetic acid, corresponding to a normalized conversion of 4-AAP of 16.35% and a normalized efficiency to HQ and its esters of 98.90% based on 103.17% accountability of products.

The product solution was subjected to further oxidation following the procedure of Example 6 except that 87.3 grams of product solution were added to the reaction flask, the temperature employed was 95°C, 25 grams of purified peracetic acid solution were added over a 30 minute period, and the reaction solution was heated for an additional 90 minute period. The initial mole ratio of peracetic acid to 4-AAP was 2.19.

The final product solution weighed 110.3 grams and contained 7.80 wt.% DAHQ, 0.05 wt.% MAHQ, 0.01 wt.% HQ, 0.01 wt.% BQ, 6.90 wt.% 4-AAP, and 0.60 wt.% peracetic acid, corresponding to a normalized conversion of 4-AAP of 53.30% and a normalized efficiency to HQ and its esters of 99.77% based on 104.03% accountability of products.

Example 15

This Example illustrates the methylation of 4-hydroxyacetophenone (4-HAP) to form p-methoxyacetophenone (PMAP).

50g (0.37 mol) of 4-hydroxyacetophenone, 51.8g (0.37 mol) of methyl iodide, and 51 g (0.37 mol) of potassium carbonate were dissolved in 55 ml or dry acetone and gently refluxed for 24 hours. After cooling the reaction mixture 200 ml of water were added to dissolve the precipitated potassium iodide. The resulting mixture was extracted three times with 200 ml of ether. The combined organic material was separated, washed with 10% sodium hydroxide dried over anhydrous potassium carbonate, filtered and evaporated. Distillation of the residue (110°C @ 2 mmHgA) afforded 50 g (ca.92% yield) of a white crystalline solid which was p-methoxyacetophenone (PMAP).

Example 16

This Example illustrated the Baeyer-Villiger oxidation of p-methoxyacetophenone (PMAP) to p-methoxyphenyl acetate (PMPA).

The procedure of Example 6 was followed except that 24.2 grams of PMAP and 0.005 gram of EDTA were dissolved in 76.8 grams of acetic acid (no acetic anhydride), 45.7 grams of purified peracetic acid solution were added over a 20 minute period, and the reaction solution was heated for an additional 60 minute period. The initial mole ratio of peracetic acid to PMAP was 1.11.

The product solution weighed 144.2 grams and contained 13.70 wt.% PMPA, 0.01 wt.% p-methoxyphenol, i.e. the monmethyl ether of hydroquinone (MEHQ), 4.30 wt.% PMAP, and 0.90 wt.% peracetic acid, corresponding to 74.40% conversion of PMAP and 99.9% efficiency to PMPA.

The PMPA may be hydrolyzed to MEHQ using the procedure of Example 13.

The procedures of Examples 6 to 16 can also be used to prepare, for example, 3-phenylcatechol from 2-hydroxy-5-phenyl-acetophenone; phenylhydroquinone from 4-hydroxy-3-phenyl-acetophenone; methylhydroquinone from 4-hydroxy-3-methyl-acetophenone; catechol from 2-hydroxyacetophenone (2-HAP); guaiacol from 2-methoxyacetophenone; 2,6-diacetoxynaphthalene and 2,6-dihydroxynaphthalene (2,6-DHN) from 6-acetoxy-2-acetonaphthone; and 4-acetoxy-4'-hydroxybiphenyl and 4,4'-biphenol from 4(4'- hydroxyphenyl) acetophenone.

It will of course be understood that the present invention has been described above by way of example, and that modifications of detail can be made within the scope of the invention.

Claims

1.   A process in which there is produced a carboxylate ester of an aromatic diol or a carboxylate ester of a mono-alkyl ether of an aromatic diol, which comprises subjecting an aromatic ketone (containing a hydroxy, alkoxy or acyloxy radical on the aromatic ring) to a Baeyer-Villiger oxidation using peracetic acid as oxidant such that the reaction mass contains no more than 0.1 wt.% of sulfuric acid based on the weight of peracetic acid initially added.

2.   The process of claim 1 in which the reaction mass contains no more than 5 wt.% of water based on the weight of peracetic acid initially added.

3.   The process of claim 1 or 2 in which the said aromatic ketone is 4-hydroxyacetophenone and the said carboxylate ester is the monoacetate ester of hydroquinone.

4.   The process of claim 1 or 2 in which the said aromatic ketone containing a hydroxy radical is prepared by contacting an ester of a phenolic compound and carboxylic acid, with a Fries rearrangement catalyst.

5.   The process of both claims 3 and 4 in which the said ester of a phenolic compound is phenyl acetate, and the said Fries rearrangement catalyst is hydrogen fluoride.

6.   The process of claim 1 or 2 in which the said aromatic ketone containing a hydroxy radical is prepared by contacting a phenolic compound and an acylating agent with a Friedel-Crafts catalyst.

7.   The process of both claims 3 and 6 in which the said phenolic compound is phenol, said acylating agent is acetic acid or acetic anhydride, and the said Friedel-Crafts catalyst is hydrogen fluoride.

8.   The process of any of claims 1-7 in which the said carboxylate ester is hydrolyzed to an aromatic diol or a monoalkyl ether of an aromatic diol.

9.   The process of both claims 3 and 8 in which the said monoacetate ester is hydrolyzed to hydroquinone.

	DOCUMENTS CONSIDERED TO BE RELEVANT		EP 85307489.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 72, September – December 1950, Easton, PA W. VON E. DOERING et al. "The peracetic acid clearage of unsymmetrical Ketones" * Pages 5515-5518 * --	1	C 07 C 69/16 C 07 C 67/42 C 07 C 45/54 C 07 C 45/46 C 07 C 27/02
D,A	CHEMICAL ABSTRACTS, vol. 93, no. 1, July 7, 1985, Columbus, Ohio, USA N. HIRAO et al. "Synthesis of dihydrobenzene by oxidation of hydroxy acetophenone" page 711, column 1, abstract no. 7777n & Koen Yoshishu-Koryo, Terupen oyobi Seiyukagaku ni kansuru Toroukai, 23rd 1979, 131-3 --	1,3,4, 6,8,9	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	22-01-1986	HOFBAUER

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85307489.6

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
D,A	THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 61, July-December 1939, Easton, PA. J.H. SIMONS et al. "Hydrogen Fluoride as a Condensing Agent. VII. The Acylation of Aromatic Compounds" * Pages 1795, 1796 * ---	6,7	
A	EP - A1 - 0 060 419 (BASF) * Examples * ----	4-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl 4)

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VIENNA	22-01-1986	HOFBAUER

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